Soil phosphorus dynamics following land application of unsaturated and partially saturated red mud and water treatment residuals

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Abstract

The secondary use of P-sorbing industrial by-products as a fertilizer or soil conditioner is gaining increased attention, particularly in light of diminishing reserves of rock phosphate traditionally used to manufacture P fertilizer. This study examined applications of red mud (RM) and water treatment residuals (WTR) at two levels of P saturation (i.e. 'as received' and partially saturated) in a soil incubation and runoff plot study. When incubated with soils ranging in texture and initial P concentration, P-sorbing residuals that were less enriched with P decreased water-extractable soil P (WEP) concentration to a greater extent than more P saturated residuals. In contrast to WTR treatments, not all of the RM applications decreased soil WEP concentrations below those of the control soils. The runoff study investigated soil P dynamics when partially P-saturated RM and WTR's were surface applied to grass plots at 2 t ha^{-1} on Day 0, followed by three rainfall simulations (7 cm hr^{-1} for 30 min, Days 2, 7 and 28) and at 3 t ha^{-1} on Day 70 followed by two more rainfall simulations (Days 77 and 96). Application of residuals at these rates did not significantly increase dissolved reactive P (DRP) in runoff compared with unamended controls during the study. Forage cuttings taken 90 days after the first rainfall simulation indicated that nutrient uptake was not compromised by the application of the residuals. Overall results indicate that WTRs may be a more suitable soil amendment than RM residuals given their greater ability to reduce soil WEP across a range of soils without simultaneously increasing Mehlich-3 extractable soil P concentrations above the upper threshold limit (150 mg P kg^{-1}), and their minimal impact on plant nutrient uptake.

Key words: P filters, water treatment residual, red mud, degree of P saturation, soil incubation, rainfall runoff.

NOMENCLATURE

DRP	Dissolved reactive P (mg L^{-1})
DPS	Degree of P saturation (M3- (P/[Al+Fe]) (%)
DPSmod	Modified degree of P saturation (M3- (P/[Al+Fe+Ca]) (%)
EC	Electrical conductivity (µS/cm)
FGD	Flue gas desulfurization
LOI	Loss on ignition (%)
M3	Mehlich-3 extractant test (mg kg^{-1})
PSD	Particle size distribution (%)
RM	Red mud
RM(ar)	'As received' red mud
RM(sat)	P saturated (or partially P saturated) red mud
RS1, RS2, etc	Rainfall simulation 1, 2 etc.
TP	Total P (mg L^{-1})
WEP	Water-extractable P (mg kg^{-1})
WTR	Water treatment residuals
WTR(ar)	'As received' water treatment residuals
WTR(sat)	P saturated (or partially P saturated) water treatment residuals

Introduction

Nitrogen (N) and phosphorus (P) enrichment remains a major impairment to designated uses of fresh and coastal waters globally (Schindler et al., 2008). Significant P contributions from the agricultural sector, in particular intensive livestock and crop production, is recognized as an issue that requires particular attention (USEPA, 2010). There is therefore growing acceptance that new technologies may be needed to reduce P losses from agricultural lands (Buda et al., 2012; Sharpley et al., 2015). The use of P-sorbing industrial by-products as filter materials is a particularly attractive option (Vohla et al., 2011) and may be an inexpensive alternative to chemical amendments (McDowell and Nash, 2012). In many cases, industrial by-products with high P sorbing capacities are stockpiled or disposed to landfill with high associated costs; however their use to mitigate agricultural P-losses would be highly beneficial for producers and industry alike. Effective P-sorbing materials include mine treatment residuals such as ochre (Dobbie et al., 2009; Fenton et al., 2009; Heal et al., 2003), water treatment residuals (Callahan et al., 2002; Babatunde et al., 2009; O'Rourke et al.,

68 2012), coal combustion by-products (Callahan et al., 2002; Stout et al., 1998; Oladeji et al.,
69 2007; Agyin-Birikorang et al., 2007; Oliver et al., 2011), gypsum (Callahan et al., 2002;
70 McFarland et al., 2003; Watts and Torbert, 2009; Andrade et al., 2002; Bryant et al., 2012;
71 Uusi-Kamppa et al., 2012), hydrochars (Fei et al., 2019) and bauxite residue, also termed red
72 mud (Cusack et al., 2018; Pepper et al., 2018).
73
74 Phosphorus-sorbing, industrial by-products have been shown to decrease the loss of P in
75 surface runoff when: i) added to soils with elevated soil-test P levels (Stout et al., 2000;
76 Callahan et al., 2002; McFarland et al., 2003; Novak and Watts, 2005; Brauer et al., 2005), ii)
77 added to bio-solids (Ippolito et al., 1999) and animal manure prior to application to soil (Dao
78 and Daniel, 2002; Dou et al., 2003; Elliott et al., 2005; Torbert et al., 2005), iii) used in edge-
79 of-field filter strips designed to intercept overland flow (Dayton and Basta, 2005; Dorioz et
80 al., 2006; Uusi-Kämppä and Jauhiainen, 2010); Uusi- Kämppä et al., 2012), and iv) used as
81 in-ditch P removal filter systems (McDowell et al., 2008a; Penn, 2011; Groenenberg et al.,
82 2013).
83
84 Applying WTR's (20 t ha^{-1}) to a buffer strip down-slope of soil receiving poultry litter,
85 Dayton and Basta (2005) reported a decrease between 67 and 86% in runoff DRP compared
86 to the unamended buffer strip. Similarly, Uusi-Kämppä and Jauhiainen (2010) reported that
87 when applied to buffer strips, Fe-gypsum, and granulated ferric sulphate reduced DRP and
88 total P (TP) losses between 74 to 85 and 47 to 64%, respectively but gypsum and $CaCO_3$ did
89 not result in any changes. Other remediation techniques to treat in-stream wastewater have
90 been investigated, including filter socks (Shipitalo et al., 2012) and various reactive barriers
91 placed along field and sub-surface drains (Penn, 2011). McDowell et al. (2008b) reported that
92 backfilling tile drains with a mixture of 90% smelter slag and 10% basic slag reduced the

control DRP and TP from 0.33 to 0.09 mg DRP L^{-1} and 1.2 to 0.36 mg TP L^{-1} respectively. Treating runoff from a golf course, Penn et al. (2012) showed that a flow through system using steel and surface modified steel slag reduced DRP by approximately 31%, with the need to replenish the slags when they became P-saturated. Similarly Bryant et al. (2012) reported removal rates between 35 and 90% of soluble P (precipitated as calcium phosphate) that passed through a permeable flue gas desulfurization (FGD) gypsum barrier to intercept ditch water; however, the hydraulic capacity of the FGD material was identified as the limiting characteristic of this system.

While addition of P-sorbing amendments to inorganic and organic fertilizers may be effective in decreasing short term P runoff losses, sorbed P may accumulate on the soil in a diffuse manner making it difficult to mine and transport from P-enriched to P-deficient areas either on or off farm. There is a risk, therefore, that some future farm management practices may result in a P sink becoming a P source. In contrast, in-ditch and edge-of-field filters facilitate P entrapment on site and subsequent relocation to a P-deficient area. In order for by-products to be economical, they must be available locally, have a high P sorption capacity, and have hydraulic properties appropriate for the application (McGrath et al., 2013).

An ideal scenario for use of P-sorbing industrial residuals is that they can initially be used to adsorb P in filter drains, and once they reach a pre-determined P saturation level, they can then be removed and applied to P-deficient soils as a slow release fertilizer. Such a scenario would not only reduce P lost to runoff, but would also conserve on-site P, resulting in an overall reduction in P imports to both aquatic systems and agricultural land. However, there is a general lack of information relative to the release of P from partially or fully saturated

residuals when applied to soil, which is one of the biggest barriers to the development of industrial residuals as sustainable on-farm technology.

The objectives of this study were to i) use an incubation experiment to determine the effect of as received and partially P-saturated filter media [Red Mud (RM) and Water Treatment Residuals (WTR)] on water-extractable soil P (WEP) and soil-test P (STP) using three soil textures with three levels of STP, and ii) investigate P losses from grassland plots following application of as received and partially P-saturated RM and WTRs subjected to simulated rainfall.

Red mud or bauxite residue is a byproduct of the alumina extraction and steel manufacturing industries, and is enriched with oxides of Fe, Al and Ca (IAI, 2015) which make it a suitable medium for P adsorption. Uptake levels in the range 0.2 mg P g^{-1} for untreated (Grace et al., 2015) and 203 mg P g^{-1} for acid/heat treated (Liu et al., 2007) red mud have been reported; however recovery in the form of Ca-P is more stable and bioavailable in contrast with P associated metal cations (Melia et al., 2017; Cusack et al., 2018). Water treatment residuals typically comprise an iron / alum sludge byproduct with reported P uptake in the range 17.1 – 21.3 mg g^{-1} (Gao et al., 2013; Wang et al., 2016). Both RM and WTR's usually contain significant but varying amounts of P which has been adsorbed during their original applications (Herron et al., 2016). The amendments used in this study were selected based on their local availability, their perceived minimum risk to the environment, and their affinity to bind large amounts of P (Herron et al., 2016).

Materials and Methods

Chemical and physical analyses

Chemical and physical analyses were carried out on residuals and soils as follows: (i) electrical conductivity (EC) and pH on a 1:2 sample / water ratio, measurement by electrode; (ii) Mehlich-3 (M3) (Mehlich, 1984), plant available nutrients using 10:1 volume extractant to residual mass on undigested samples and 50:1 volume extractant to residual mass on digested samples, analysis on Spectro Arcos ICP, acid digestion to USEPA method 3050B (USEPA, 1996); (iii) total N and C using high-temperature combustion of approximately 30 mg sample, analysis using Elementar varioMAX CN; (iv) loss on ignition (LOI) using muffle furnace to 360 °C and gravimetric measurement; (v) dissolved reactive P (DRP) by filtration (0.45 µm) and colorimetric analysis using the method of Murphy and Riley (1962); (vi) WEP by shaking 10:1 deionized water volume to air dried sieved (< 2 mm) samples, filtration (0.45 µm) and colorimetric analysis (McDowell and Sharpley, 2001); (vii) total P (TP) by digestion (2 h at 400 °C) with a mixture of concentrated nitric and hydrochloric acid (Leytem and Kopombblekou, 2009) followed by colorimetric analysis; (viii) water-holding capacity by saturating a 50-g soil sample with deionized water and reweighing after 48 h of free drainage (Bond et al., 2006); (ix) initial water content by drying at 105 °C for 24 h; and (x) soil particle size distribution (PSD) using the hydrometer method (ASTM F1632, 2010).

Residual characterization and preparation

All samples (n=3) were dried at 55 °C and ground to pass a 2 mm sieve before being analysed for: (i) pH; (ii) digested and undigested M3 -P, potassium (K), calcium (Ca), magnesium (Mg), sulphur (S), sodium (Na), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), boron (B) and aluminium (Al); (iii) total N and carbon (C); and (iv) LOI. In addition, the following parameters were determined for the 'as received' RM [RM(ar)] and WTR [WTR(ar)] only (i) EC, (ii) WEP, (iii) water-holding capacity, and (iv) initial water content of air dried residuals. The maximum P sorption capacities (P_{max}) of the RM(ar) and WTR(ar)

were determined by the method of Olsen and Watanabe (1957) on samples which were air-dried for 7 days and sieved to < 6 mm. Residuals were added to between 25 and 1000 mg L^{-1} P solution (1:100 residual mass to solution volume ratio), shaken end-over-end for 1 h, centrifuged (4750 rpm for 10 min at 25°C) and analyzed for DRP within 24 h.

In order to fully or partially P-saturate the RM and WTR residuals [RM(sat), WTR(sat)], a method based on that used by Oliver et al. (2011) was used, where a known mass of air-dried residual material was packed in a 25-L reservoir, which had a perforated base. Mesh and wire wool were placed between the base and the residual media to prevent particles falling through. The reservoir was suspended above a second 40-L reservoir, which was filled with approximately 35 L of synthetic DRP solution that had a target concentration of 50 mg L^{-1}. The liquid was continuously circulated from the lower to the upper reservoir using a submersible pump thereby saturating the media in the upper reservoir (Fig. 1). Phosphorus was replenished by adding the required concentration of P solution to the lower reservoir to maintain the target concentration. Saturation took place over 4 days, following which the residual was rinsed with deionized water for 2 h before being air-dried.

Treatments

Five treatments were examined in both the laboratory incubation (Experiment 1) and plot-runoff (Experiment 2) experiments as follows: control (soil only / unamended grassed plot); amendments of RM(ar); RM(sat); WTR(ar); and WTR(sat).

Incubation study (Experiment 1)

Three soils from northwest Arkansas ranging in texture were used in the incubation study. Captina silt-loam (fine-silty, siliceous, active, mesic Typic Fragiudult) and Roellen silty-clay-

192 loam (fine, smectitic, thermic Vertic Epiaquoll) soil was collected from the top 10 cm of the
193 Animal Physiology Research Farm in Fayetteville, Arkansas (36°5′50″N, 94°10′44″W) and a
194 Linker fine-sandy-loam soil (fine-loamy, siliceous, semiactive, thermic Typic Hapludult)
195 collected from the top 10 cm of the Kibler Vegetable Research Station near Alma, Arkansas
196 (35°22′43″N, 94°13′58″W). All soil samples were air-dried, crushed to pass a 2 mm sieve,
197 and soil M3-P, WEP, pH, field moisture capacity, and soil particle-size-distribution were
198 determined.
199
200 Each soil (n=3) was amended with P (as KH_2PO_4) to achieve three M3-P levels, low (target
201 50 mg kg^{-1}), medium (target 200 mg kg^{-1}), and high (target 550 mg kg^{-1}) after McDowell et
202 al. (2011). Once amended all soils were watered to field capacity, allowed to air dry for one
203 week before being wet again to ensure equilibration between P and the soils. After a further 8
204 weeks, residuals were added at a rate equivalent to 5 t ha^{-1} to 200 g of sieved (< 2 mm), air-
205 dried soil, placed in 200 mL polypropylene containers, and (considering depth of rainfall and
206 overflow interaction as the upper 5 mm of soil; Ahuja et al., 1981) mixed thoroughly.
207 Deionized water was added to achieve approximately 80% of field moisture capacity
208 (representing in situ field moisture conditions) and the mixture was packed to an approximate
209 field-representative bulk density of 1.3 g cm^{-3}.
210
211 The containers were incubated at 20 ± 2°C for 90 days during which time they were weighed
212 at weekly intervals and distilled water added to ensure the in situ field moisture content of the
213 mixture was maintained. At various intervals into the 90-day incubation, a 10 g sub-sample
214 was collected from each container and analyzed for WEP at 7, 21, and 90 days after the start
215 of the incubation period. After 90 days, the incubated soils were destructively sampled, oven
216 dried at 40 °C for 72 h, and crushed to pass a 2 mm sieve before being analyzed for pH, EC,

and M3-P, -Ca, -Fe, and, –Al. Degree of P saturation (DPS) was calculated by dividing M3-P by the sum of M3-Al, -Fe (Maguire and Sims, 2002) and modified DPS (DPS_{mod}) by dividing M3-P by the sum of M3-Al, -Fe and -Ca.

Runoff study (Experiment 2)

Site characterization

Sixteen plots (1 by 2 m) were constructed within a 0.1 ha grassed area at the University of Arkansas Research Farm (36°5′48″N, 94°10′27″W) in northwest Arkansas, USA. The plot layout and construction followed the National Phosphorus Research Project Protocol (2015) and that described by Sharpley and Kleinman (2003). All plots had long axes in the direction of the site slope and were hydraulically isolated by driving steel edging into the soil (50 mm above and below soil surface). Each plot was instrumented with a runoff collection channel at the bottom of the slope. Following construction, plots were allowed a 10-day recovery period from any disturbance caused by installation and the grass was cut to a height of 50 mm before application of the residuals and initial rainfall simulation. Within the 16 plots, treatments were randomly assigned in two blocks (n = 2) with the exception of RM(ar) and WTR(sat) treatments where n = 3.

Soil cores were collected from an area within the site that had uniform slope (2.75 ± 0.6 %) along the length and negligible slope across the width of the runoff plots. The samples were tested for M3-P (115 ± 5.2 mg kg^{-1}), WEP (20.5 mg kg^{-1}), pH (6.54 ± 0.2), and PSD (42.2% sand, 51.2% silt and 6.6% clay). The soil surface texture at the site was confirmed to be silt loam.

Rainfall simulations

Rainfall simulations were conducted using a rainfall simulator designed to specifications described by Humphry et al. (2002) with a single TeeJetTM ½HH-SS50WSQ positioned at the center approximately 3.05 m above the soil surface (National Phosphorus Research Project, 2015). The simulator was calibrated to produce a rainfall intensity of 7 cm h^{-1} and both rainfall intensity and coefficient of uniformity (85% uniformity) were verified at the beginning of each rainfall simulation event. The rainfall simulator frame was designed so that two plots could be subjected to rainfall at the same time. The source of the simulated rainwater had DRP < 0.005 mg L^{-1}, TP < 0.020 mg L^{-1}, and a pH of 8.1±0.2. These parameters were measured immediately prior to each event and daily precipitation was measured for the duration of the experiment. Simulated and natural precipitation were measured daily for a period of 4 weeks before and 12 weeks after the study (Fig S1).

Residuals (Table 1) were broadcast by hand on Days 0 and 70 at rates of 2 and 3 t ha^{-1}, respectively. Rainfall simulations were conducted on Days 2, 7, and 28 (RS1, RS2 and RS3, after the first application of residuals) and Days 77 and 96 (RS4 and RS5, after the second residuals application). Runoff was deemed to have initiated once a constant stream of water flowed over the lip of the collection trough, at which time simulated rainfall continued for 30 min. All runoff was collected and the total volume determined by weight. A subsample was immediately transported to the laboratory, filtered (0.45 µm), and stored at 4°C until TP and DRP analyses were carried out within 7 days of collection (n=3).

Soil and vegetation samples

Six months after application of the first residuals, soil samples were collected from the top 10 cm from each plot and tested for WEP, pH, EC, and M3-P, -Ca, -Fe, and -Al. Prior to the

final rainfall simulations (day 96), vegetation samples were cut to 50 mm, dried for 7 days at 55 °C, and analyzed for total P, K, Ca, Mg, S, Na, Fe, Mn, Zn, Cu, B, and Al.

Statistical analyses

Data for soil M3-P and soil WEP in the incubation study, runoff TP and DRP loads, soil M3 – P, -Ca, -Fe, and -Al from rainfall simulation plots and forage –P, -K, -Ca, -Mg, -S, and –Na concentrations were tested for normality and homogeneity of variance to ensure compliance with Gaussian distribution requirements and analyzed using one-way analysis of variance (ANOVA) in SPSS (IBM SPSS Statistics 20 Core System). Comparisons between means were made using Tukey adjustments to *p*-values and statistical results were considered significant and are reported at the 0.05 level.

Results and Discussion

Residuals

The average pH of the RM residuals (7.54±0.08) was similar to that of the WTR (7.26±0.02), however the EC of the WTR(ar) was much higher than that of the RM(ar) (767 and 11.4 µS/cm respectively), which may be partly due to the much higher concentrations of aluminium in the alum based WTR (Table 1). With the exception of Al, the RM residuals had higher metal concentrations than the WTR, in particular Ca which is added as $Ca(OH)_2$ during the production process (Herron et al., 2016). The TP concentration of the undigested RM(ar) (593 mg kg^{-1}) was much higher than that of the WTR(ar) (9.6 mg kg^{-1}) and this differential was even greater between the RM(sat) and WTR(sat) (2,903 and 75 mg kg^{-1} respectively). Similarly the P adsorption capacity of the RM(ar) residuals (16.9 g kg^{-1}) was higher than that of the WTR(ar) (2.85 g kg^{-1}), even though the WTR(ar) had similar concentrations of Fe and much higher concentrations of Al. It is likely, therefore, that the

very high Ca concentrations in the RM(ar), which had a pH >7, provided cationic exchange sites and significantly enhanced its ability to sorb P, likely in the form of HPO_4^{2-}, at this pH (Shaheen et al., 2009). Similarly, the WEP of the RM(ar) was higher than that of the WTR(ar) (0.57 and 0.06 mg kg^{-1}, respectively) reflecting the higher amounts of P adsorbed by the RM residuals, which was subsequently available for desorption. With the exception of Al, the metal concentrations of the digested RM were generally much higher than those for digested WTR, in particular Ca, Na, Fe, K, Zn, and Cu. The digested P concentrations of the RM(ar) and RM(sat) (41,735 and 58,850 mg kg^{-1}, respectively) were also significantly higher than those of the WTR(ar) and WTR(sat) (1,162 and 5,287 mg kg^{-1}, respectively). This is most likely due to the higher combined residual Fe and Ca concentrations in the RM, which were greater than the digested Al concentrations in the WTR (Table 1).

Incubation study

In general, soil WEP in the unamended controls increased with increasing M3-P concentrations and with increasing DPS levels (Fig. 2). The sand soil exhibited the highest WEP concentrations, followed by silt and clay soils and the differences to which the WEP increased are influenced by the relative silt and clay content of the soils (Table 2) and by the relative soil M3 –Fe and –Al concentrations (Tables S1-S3). The largest average increase in WEP across all sampling times (7, 21, and 90 days) was measured for the sand soil, which increased from 9.1 (low M3-P) to 315 mg kg^{-1} (high M3-P), likely due to its reduced ability to adsorb dissolved P (Zhang et al., 2002). Increases for the silt and clay soils were not as pronounced (8.3 to 167 and 0.2 to 75.7 mg kg^{-1} for low and high M3-P, respectively) (Fig. 3).

Application of RM(ar) significantly decreased soil WEP compared to unamended controls for all soils at all M3-P concentrations, except for the clay –low M3-P treatment; however, this

316 soil had the lowest initial WEP concentration with an average of 0.17 mg kg^{-1} (Fig. 3).
317 Conversely application of RM(sat) increased WEP for sand, silt, and clay -low, and clay -
318 medium treatments compared to unamended controls but reduced it for all other treatments,
319 although these differences were significant only in the cases of clay –low and –medium, and
320 sand and silt – high soils. This would imply that the RM residuals were partially but not fully
321 saturated prior to application, as they had the capacity to adsorb P from medium and high
322 M3-P soils. The reason for the WEP increase in the low M3-P soils is likely related to the
323 high P concentrations in the RM residuals, which in turn are related to their very high Ca
324 concentrations (Table 1). It is possible that with such high Ca concentrations, precipitation as
325 well as desorption of P, may occur particularly at elevated pH levels (Rietra et al. 2001),
326 which may result in an increased long-term P pool, particularly in alkaline soils. In general,
327 application of RM residuals only marginally increased soil pH over the 90-day incubation
328 although a maximum increase of 36% over the control was measured for the medium M3-P
329 clay soil (Table S3).
330
331 Application of WTR(ar) and WTR(sat) reduced WEP compared to the unamended controls
332 for all soil textures at all M3-P levels, except for the clay–low-WTR(sat) combination, where
333 the average WEP slightly numerically increased from 0.2 to 0.3 mg kg^{-1}. This would imply
334 that the WTR(sat) residuals were partially rather than fully saturated, as was the case for
335 RM(sat). It should be noted that although the WTR(sat) treatments did not differ
336 significantly from the RM(sat) treatments for WEP reduction in the high M3-P soils, they
337 differed for medium and low M3-P soils, demonstrating better overall P sorption capacity
338 across the range of soil types studied.
339

340 Dayton and Basta (2005) reported similar decreases in soluble P of up to 28, 58, and 87%
341 from high M3-P soils (315 mg kg^{-1}) treated with WTRs at rates of 25, 50, and 100 g kg^{-1},
342 respectively. These results are also largely in agreement with other previous work, which
343 reported that application of alum-based WTRs to (i) poultry litter (Codling et al., 2000), (ii)
344 sandy soils amended with municipal bio-solids and triple superphosphate (Elliott et al.,
345 2002), and (iii) P-enriched coastal plain soils (Novak and Watts, 2005) resulted in substantial
346 reductions in water soluble P. Codling et al. (2000) reported that water soluble P
347 concentrations were typically reduced to less than 10 mg kg^{-1} for three long term poultry litter
348 amended soils after a 14-day incubation for WTR and iron-rich residue mixed at rates of 25 g
349 kg^{-1}soil, but generally WTR was more effective at immobilizing water soluble P. Similarly
350 Elliott et al. (2002) reported that alum based WTR was more effective than either Ca-WTR or
351 Fe-WTR in reducing soluble P in Immokalee soils. Novak and Watts (2005) reported that
352 WTR application to P-enriched sandy soils at rates of 1, 2, 4, and 6% ww^{-1} resulted in
353 proportionally higher reductions of water soluble P than soil M3-P, with near linear
354 reductions of both as WTR application rates increased.
355
356 After the 90-day incubation, RM treatments increased M3-P of all soils above those of their
357 corresponding unamended controls and these differences were significant for all RM(sat)
358 treatment combinations, and for the RM(ar)-clay-low and –medium treatment combinations.
359 Thus, application of RM residuals, whether unsaturated or partially saturated resulted in
360 increased soil M3-P concentrations which in all cases were far greater than the upper
361 threshold limit of P application in P loss risk assessment (i.e., 150 mg kg^{-1}) in the Mid-
362 Atlantic region of the USA (Sims et al., 2002; Novak and Watts, 2005). The high M3-P
363 concentrations in the incubated soil following RM treatments, reflect the much higher P
364 concentrations of the RM when compared to the WTR residuals, and these in turn are

reflective of the much higher Ca concentrations in the RM residuals (Table 1). Unlike RM, all WTR treatments reduced M3-P concentrations for all high M3-P soils when compared to the unamended controls; however, they also did not reduce these to below the 150 mg kg^{-1} threshold and reductions were not significant. In contrast, all WTR treated low and medium M3-P soils remained below the 150 mg kg^{-1} threshold and there were no significant differences between treatments after 90 days incubation (Fig. 3, Tables S1-S3). Results of this study indicate that application of unsaturated or partially saturated WTRs are generally more effective than corresponding RM applications in reducing soil WEP in a variety of soil textures and M3-P concentrations without major negative impact on the agronomically beneficial soil-P levels.

The DPS (van der Zee and van Riemsdijk, 1988) was observed to be a good predictor of sand and clay soil WEP for low and medium M3-P soils treated with WTRs, but less so for the high M3-P soils (Fig. 4). Sand and silt soil WEP had relatively similar responses to DPS, with a slower response for the clay soils, probably because of its higher buffering capacity. The DPS for WTR treatments did not exceed 20% and greatly differed from the RM treatments, in which DPS was never less than 100% and as high as 1800% for the medium-P-silt treatment combination (Fig. 4). In addition, the correlations between DPS and soil WEP for RM applications were significant ($p < 0.05$) only for clay low, sand medium, and silt high soils. Thus, DPS was not a reliable indicator of soil WEP for RM treatments, likely due to large increases in Ca concentrations (average 9, 6, and 4 fold for the clay-loam, sandy-loam, and silt-loam soils, respectively) following RM application. In order to reflect the influence of Ca following RM applications, a modified DPS (DPS_{mod}) was used to predict soil WEP [i.e., DPS_{mod} = (M3–P/[[Al + Fe + Ca])] for all treatment combinations. This resulted in significant linear correlations (and maximum $DPS_{mod} < 30\%$) for all RM treatments (Fig. 4a),

with no impact on correlations for soils receiving WTR applications, reflective of the minor Ca reductions in these soils (Tables S1-S3). The improved correlations for the RM treatments further validate that assumption that elevated Ca concentrations in the RM provides a reactive P binding surface which significantly increases its P sorption capacity.

Soil EC was poorly correlated with WEP for all treatment combinations (R^2 ranged from 0.03 to 0.44), thus soil EC was a poor predictor of soil WEP for both RM and WTR applications. However, RM application generally increased soil EC by at least one order of magnitude for all soil textures and at all M3-P levels probably as a result of the higher salt metal concentrations in the RM compared to the WTR residuals, in particular Mg, Na, Zn and Cu (Table 1). In contrast WTR applications had minimum effect on soil EC throughout the study even though the untreated WTR residuals had a much greater EC themselves than the RM material.

Runoff study

Runoff DRP and TP loads for all treatments were greatest during the first and fourth rainfall simulation events (i.e., RS1 and RS4, respectively), which coincided with residual applications on Day 0 at 2 t ha^{-1} and on Day 70 at 3 t ha^{-1} (Fig. 5). Given that DRP comprised >85% of the TP load in runoff (Fig 6), it is likely that desorption was the main mechanism of P release, however, increased P loads from the control plots also coincided with the rainfall events and it is also possible that some soil P mineralization processes might have contributed to the total P load.

Although there were no significant differences between treatments for cumulative DRP and TP loads (Fig 6), RM(ar) treated soils resulted in cumulative reductions of DRP (23.2%) and

TP loads (18.1%) when compared to control soils. In contrast, RM(sat) treated soils increased DRP and TP loads by 22.8 and 36.9%, respectively. These cumulative increases, however, were as a result of the second residual application followed by two additional rainfall simulations (RS4 and RS5; Fig. 5). It is also worth noting that while the WEP of the RM(ar) and WTR(ar) residuals used for the Day 70 application were slightly lower than those used for the Day 0 application, this was not the case for RM(sat) and WTR(sat) (Table 3). Application of WTR(ar) also reduced cumulative DRP and TP loads below those of the control soils, although these reductions were smaller (10.9 and 7.6%, respectively) than for corresponding RM(ar) applications (Fig. 6). However, WTR(sat) also reduced DRP and TP loads by similar amounts (9.5 and 8.8%, respectively) and although these residuals were partially and not fully saturated when applied to the soil, they did not contribute to the P load in runoff. Previous studies have focused on the use of residuals to bind P in high-STP soils (Anderson et al., 1995; McFarland et al., 2003; Novak and Watts, 2005). McFarland et al. (2003) observed that alum amendments decreased DRP concentrations from 0.66 to 0.07 mg L^{-1} in simulated runoff from plots that had historically been amended with dairy slurry.

Six months after application of residuals to the grass plots, the differences between treatments within each group of results were not significant (Table 4). Soil WEP (0-10 cm depth) was lower than the controls for all residual applications, except for the RM(sat) treatment, where a slight increase (1.4%) was measured. The largest decreases were for the WTR(sat) (21.9%) and WTR(ar) (21.4%) treatments. With the exception of RM(ar) and WTR(sat), soil M3-P increased slightly for all treatments compared with the control soils while application of RM(ar) resulted in a 10.9% increase in soil M3-Fe and surprisingly a 21.9% increase in M3–Al compared to the controls. Soil EC and pH were largely unaffected by the residual applications compared to the controls six months after the first residual application, except

for the WTR(ar) where soil EC decreased by 11.9% (Table 4). In an overall sense however application of the residuals to the grass plots did not significantly alter the soil chemistry or WEP six months after application.

With the exception of RM(ar), all treatments slightly increased forage-P concentrations compared to the unamended control, although these differences were not significant (Table 5). Similarly the average forage -K, -Ca, -Mg, -S and -Na concentrations did not change significantly from those of the control soils following application of residuals. The average forage -Fe concentrations measured in plots that received the RM(sat) (240 mg kg^{-1}) treatment combinations were almost double that of the unamended control (128 mg kg^{-1}), while average forage-Fe concentrations decreased for the WTR(sat) (79 mg kg^{-1}) treatment relative to the unamended control but the differences were not significant. The average forage-Al concentrations in plots that received the RM(ar) (107 mg kg^{-1}) and WTR(sat) (116 mg kg^{-1}) treatments, were almost three times greater than those in the unamended control (29 mg kg^{-1}), and only the RM(sat) treatment resulted in a slightly reduced forage-Al concentrations (21 and 27 mg kg^{-1} respectively) relative to the unamended control but the differences were not significant. In general, these results indicate that the impacts of the residuals on forage composition were not significantly different from the control soil.

Conclusions

Application of spent RM and WTR residuals to soils as P immobilizing agents may represent an opportunity for agriculture and industry alike. The RM residuals which had high metal concentrations, in particular Ca were effective in reducing WEP from high M3-P soils but were less effective for medium and low M3-P soils. However the initial high P concentration of the RM residuals and the resultant elevated M3-P soil concentrations for all soil types after

90 days incubation may increase the long term P pool and consequent risk of P losses. In comparison application of WTR residuals did not generally result in elevated soil M3-P concentrations and were also successful in reducing soil WEP not only from high but also from medium and low M3-P soils. In general the P losses in runoff were not adversely affected by the surface application of either the RM or WTR residuals to the grassed plots with no significant differences for the DRP and TP loads between controls and RM and WTR applications. Although there were no significant adverse impacts on the soil chemistry or on forage concentrations, six months and 90 days, respectively, after RM and WTR applications, it is possible that metal leaching, particularly from the RM, may occur in neutral or slightly alkaline soils. Overall, the results of the soil incubation and field studies indicate WTR's may be more suitable than RM residuals given their greater ability to reduce soil WEP across all saturation levels in each soil texture and initial M3-P concentrations.

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Declarations of interest

None

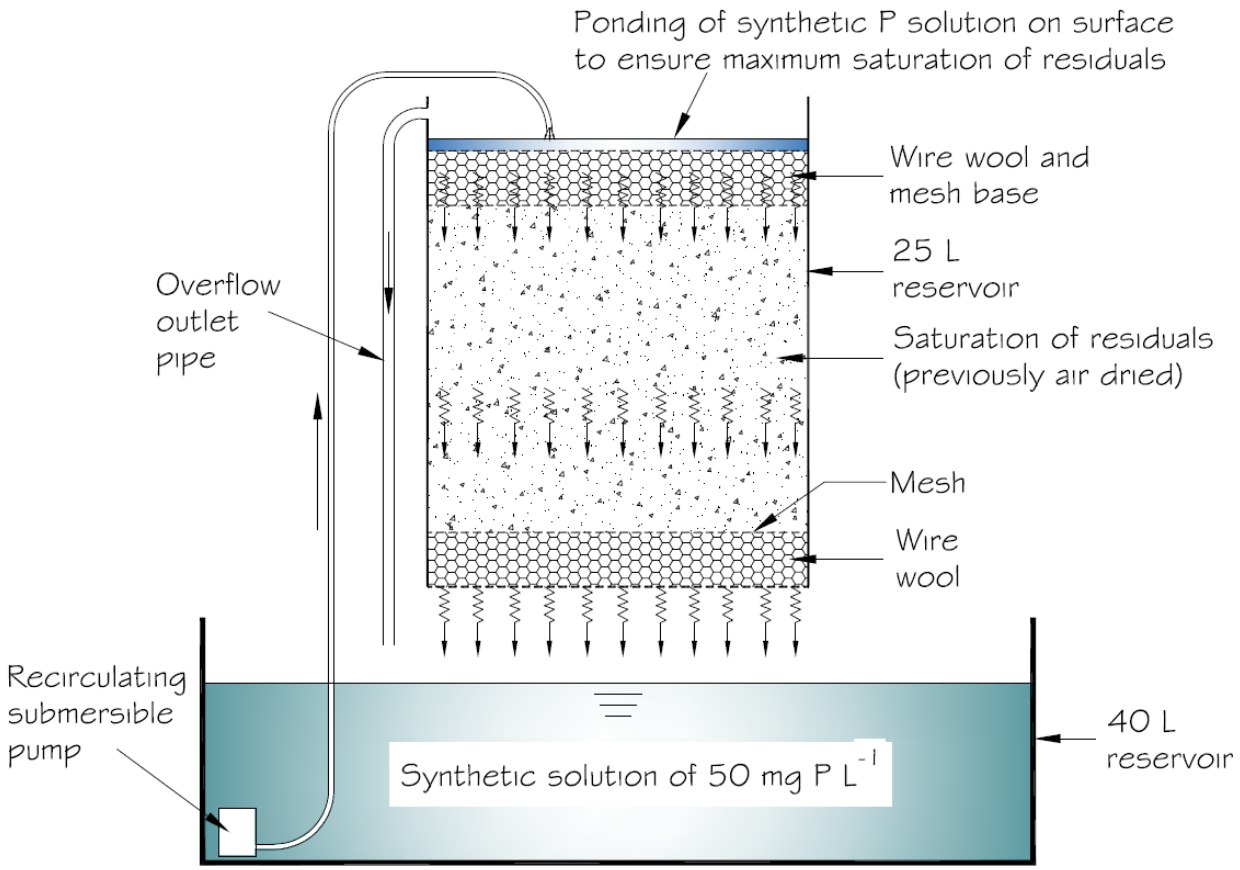

Fig. 1 Schematic diagram of laboratory setup to increase P concentrations of residuals. (Not to scale).

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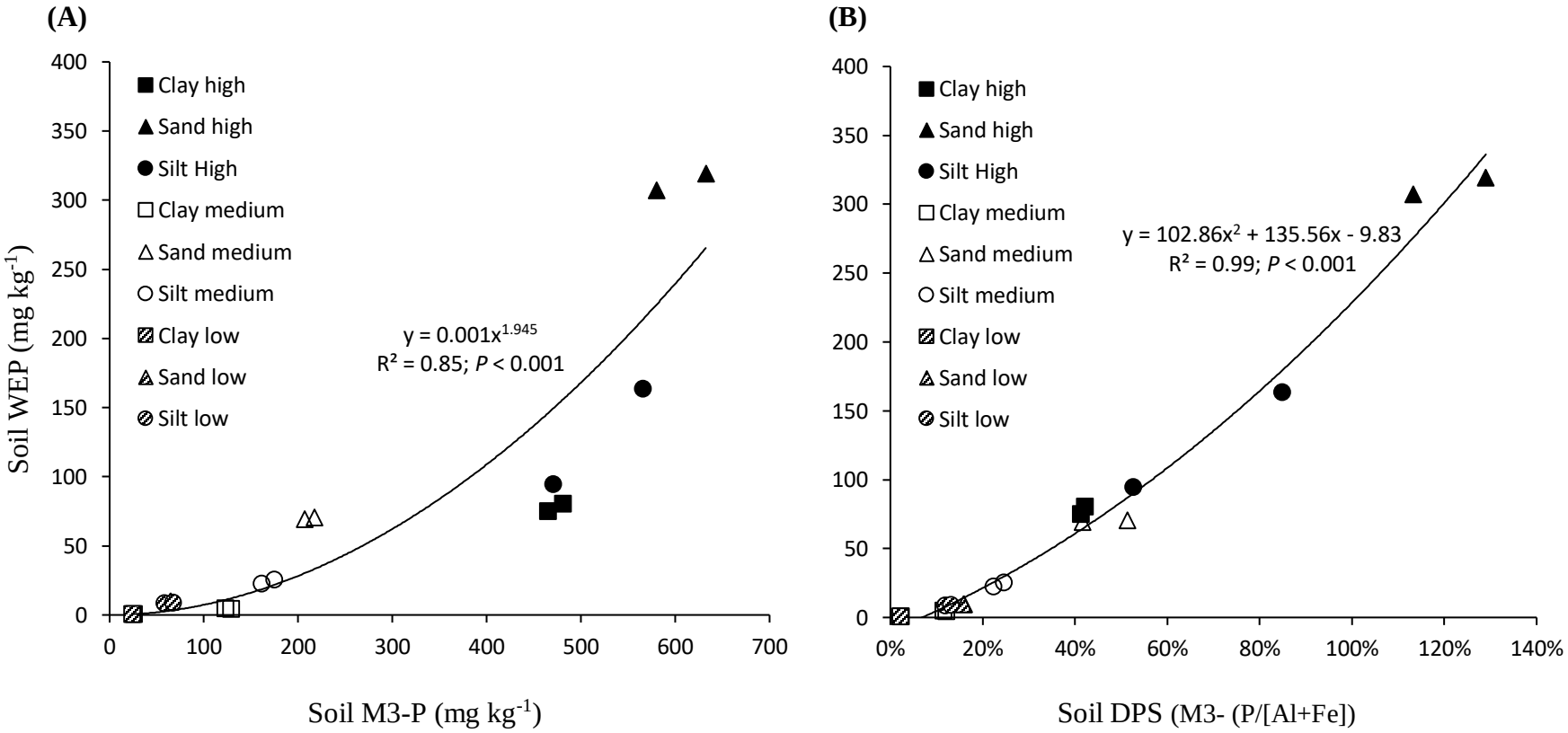

494 **Fig. 2** Soil WEP versus M3-P [Fig 2(A)] and DPS [Fig 2(B)] in unamended control soils after 90 days incubation at 20 ± 2 °C. The soils
495 used were Roellen silty-clay-loam (clay), Linker fine-sandy-loam (sand) and Captina silt-loam (silt), and were P-enriched on day 0 to
496 achieve target M3-P concentrations of 550 mg kg^{-1} (high), 200 mg kg^{-1} (medium) and 50 mg kg^{-1} (low). Lines represent best fit analysis
497 with correlation coefficients (R^2) and significance (*p*) indicated.
498

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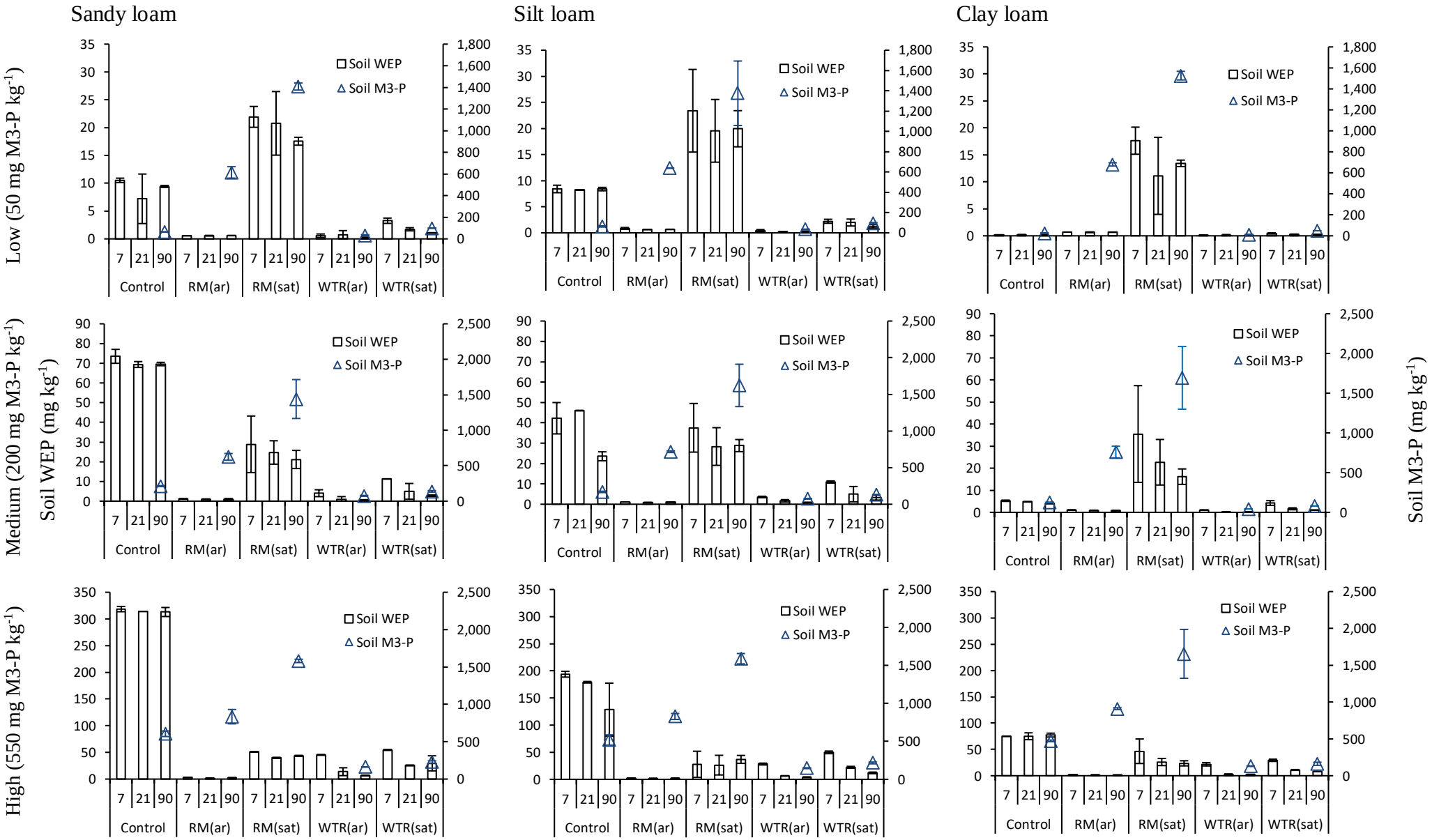


Fig. 3 Water extractable P (WEP) (days 7, 21 and 90) and Mehlich3-P (M3-P) (day 90) of P enriched soils with initial low (50 mg M3-P kg^{-1}), medium (200 mg M3-P kg^{-1}) and high (550 mg M3-P kg^{-1}) P content. 'As received' and 'partially saturated' Red Mud [RM(ar), RM(sat)] and Water Treatment Residuals [WTR(ar), WTR(sat)] were surface applied to all soils (day 0, 5 t ha^{-1}) in incubation experiment. Error bars indicate SD, n=3.

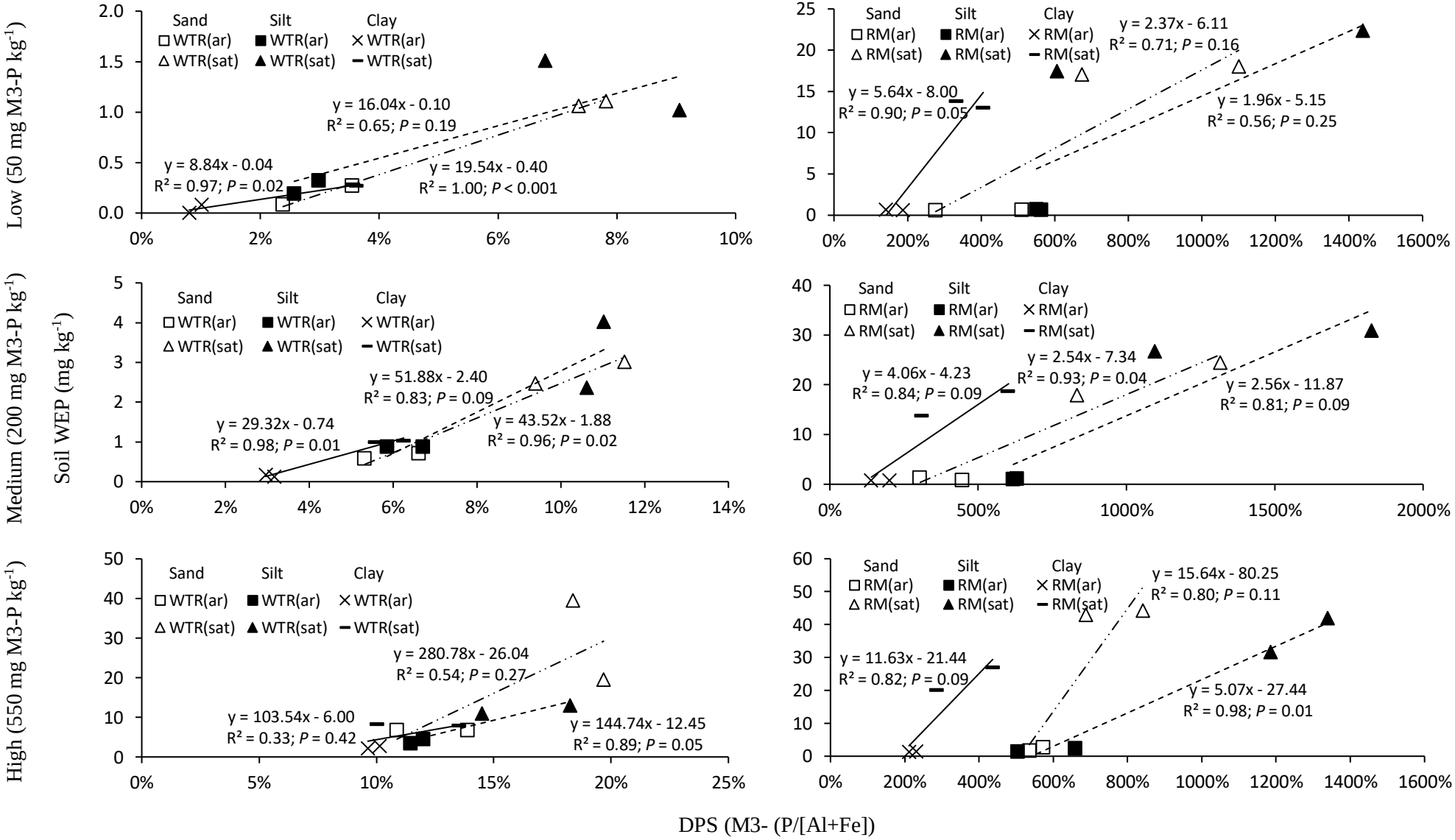


Fig. 4 Relationship between degree of P saturation (DPS) and soil water extractable P (WEP) for sandy, silt and clay loam soils with initial low (50 mg M3-P kg^{-1}), medium (200 mg M3-P kg^{-1}) and high (550 mg M3-P kg^{-1}) P content. 'As received' and 'partially saturated' Red Mud [RM(ar), RM(sat)] and Water Treatment Residuals [WTR(ar), WTR(sat)] were surface applied to all soils (day 0, 5 t ha^{-1}) and incubated for 90 days prior to analysis. Lines represent a least squares correlation analysis with correlation coefficients (R^2) and significance (p) indicated.

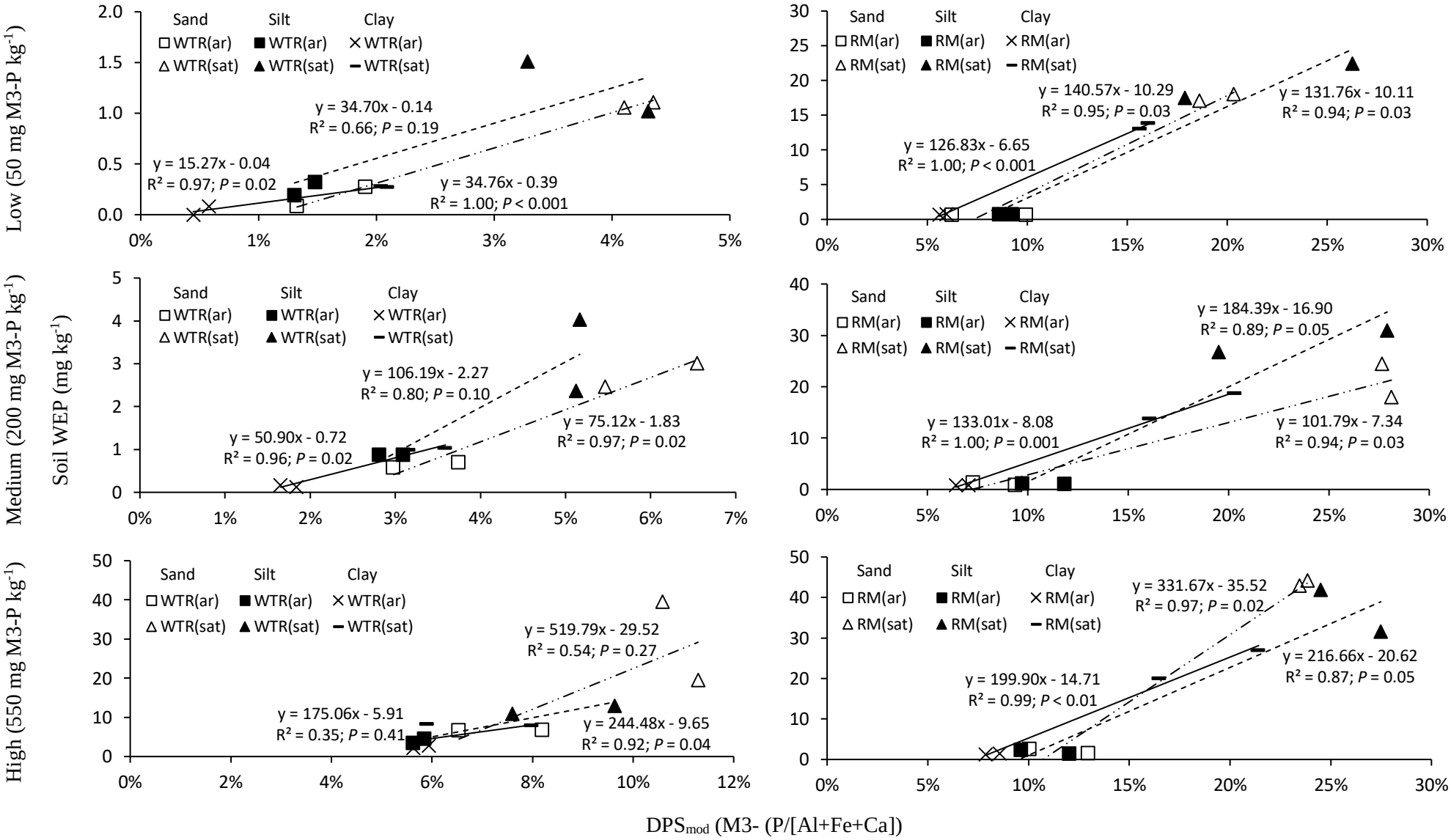
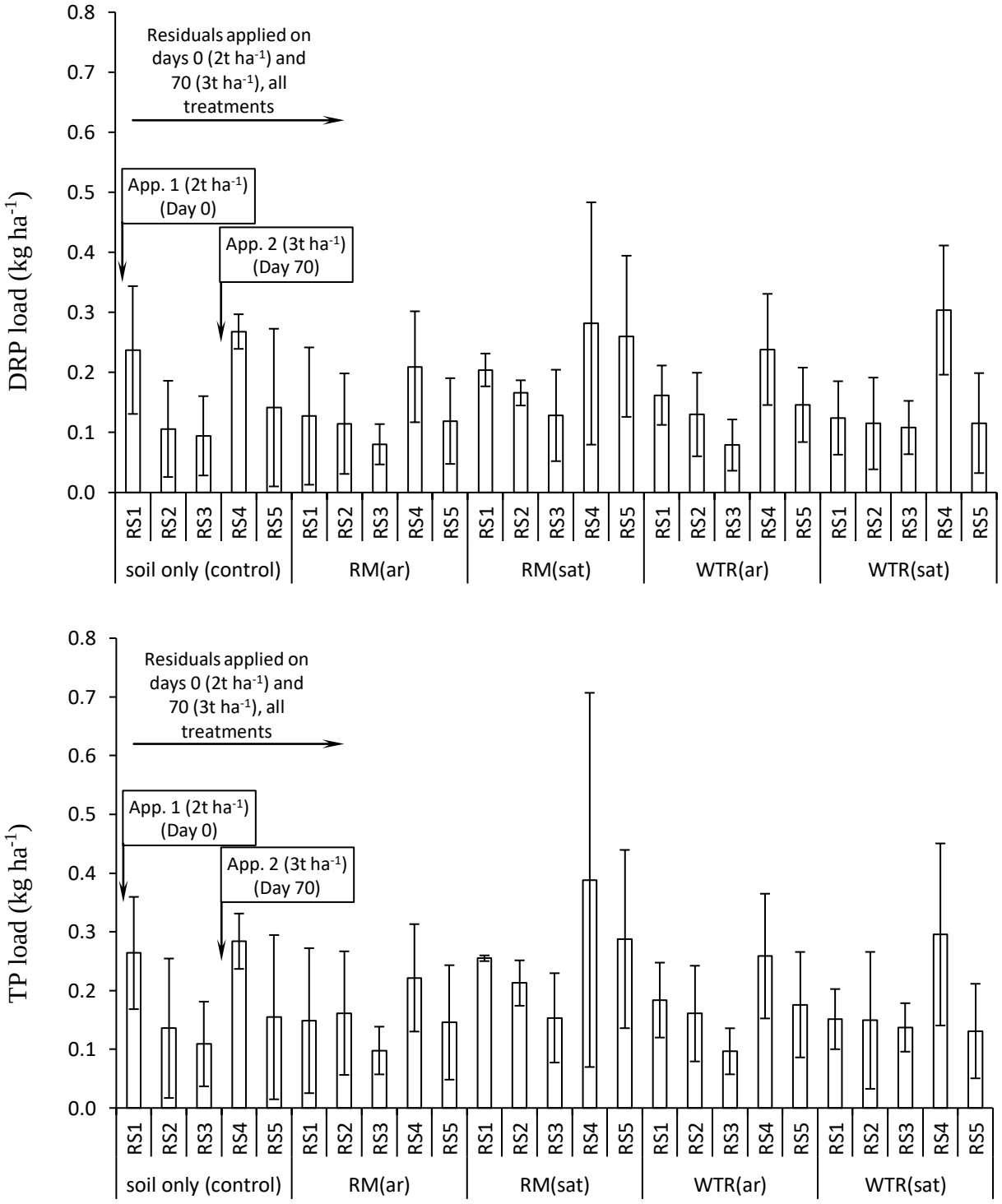


Fig. 4a Relationship between modified degree of P saturation (DPS_{mod}) and soil water extractable P (WEP) for sandy, silt and clay loam soils with initial low (50 mg M3-P kg^{-1}), medium (200 mg M3-P kg^{-1}) and high (550 mg M3-P kg^{-1}) P content. 'As received' and 'partially saturated' Red Mud [RM(ar), RM(sat)] and Water Treatment Residuals [WTR(ar), WTR(sat)] were surface applied to all soils (day 0, 5 t ha^{-1}) and incubated for 90 days prior to analysis. Lines represent a least squares correlation analysis with correlation coefficients (R^2) and significance (p) indicated.



512 **Fig. 5** Average dissolved dissolved reactive P (DRP) and total P (TP) load in runoff during
513 simulated rainfall events. Rainfall simulations RS1, RS2 and RS3 were conducted on days 2, 7
514 and 28 after the first application of residuals and rainfall simulations RS4 and RS5 were
515 conducted 7 and 26 days (days 77 and 96) after the second application. Residuals applied at the
516 rates indicated were 'as received' and 'partially saturated' red mud [RM(ar), RM(sat)] and water
517 treatment residuals [WTR(ar), WTR(sat)]. Error bars indicate SD, n=3.

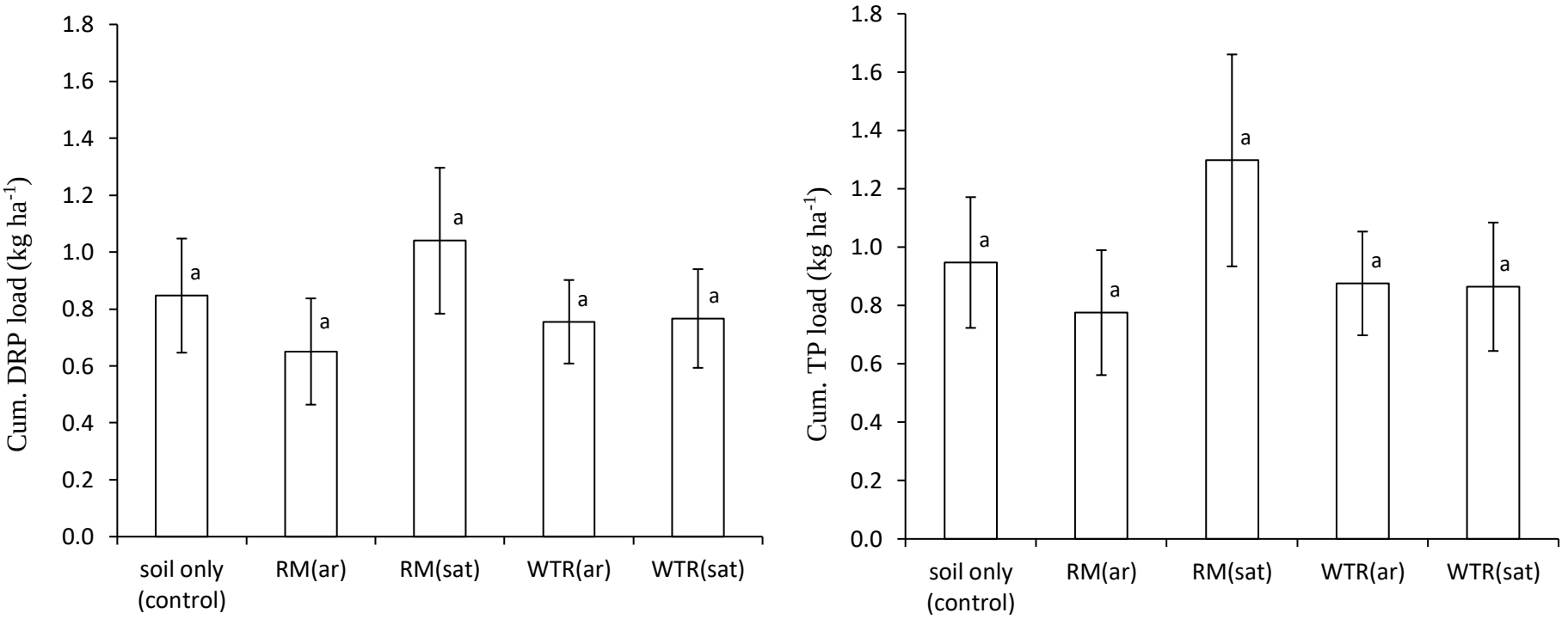


Fig. 6 Cumulative dissolved reactive P (DRP) and total P (TP) loads in runoff for five simulated rainfall events. Residuals applied were 'as received' and 'partially saturated' red mud [RM(ar), RM(sat)] and water treatment residuals [WTR(ar), WTR(sat)]. Error bars indicate SD, n=3. Means with the same letter are not significantly different ($p < 0.05$).

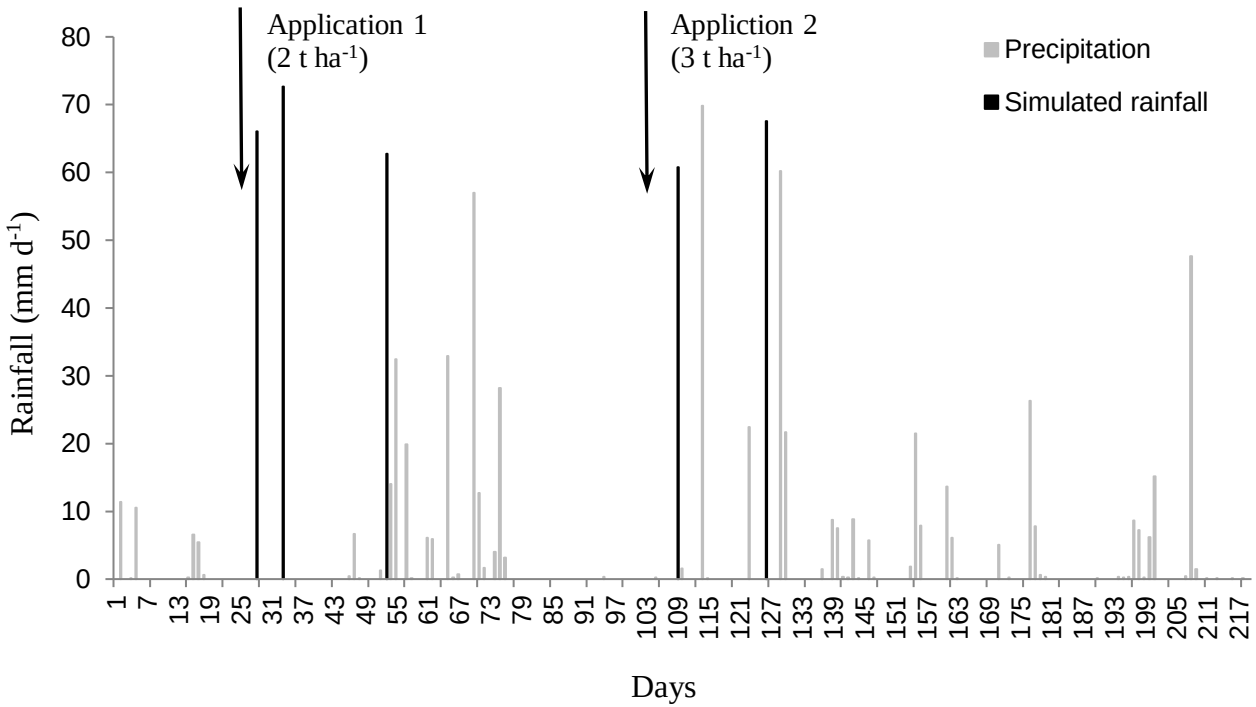


Fig. S1 Daily precipitation and simulated rainfalls (average for all plots on day of simulations) for the duration of the runoff study. Red mud (RM) and water treatment residuals (WTR) were applied at the times and rates indicated.

543 **Table 1** Characteristics of residuals used throughout the study (n=3, standard deviation in parentheses)

Residual	pH	EC	N	C	LOI	WEP	Water holding capacity	Initial water content of air dried residuals	Max P sorption capacity (< 6 mm)
		(µS/cm)	(%)	(%)	(%)	(mg kg^{-1})	(kg water kg $soil^{-1}$)	(%)	(g kg^{-1})
RM(ar)	7.6 (0.2)	11.4 (0.6)	0.1 (0.0)	4.1 (0.1)	12.7 (0.4)	0.57 (0.04)	644 (24)	30 (1.4)	16.9 (0.8)
RM(sat)	7.5 (0.3)		0.1 (0.0)	3.7 (0.1)	11.9 (0.5)				
WTR(ar)	7.2 (0.1)	767.0 (36.8)	1.3 (0.1)	9.5 (0.2)	28.3 (0.9)	0.06 (0.01)	465 (18)	40 (1.9)	2.85 (0.2)
WTR(sat)	7.3 (0.2)		1.2 (0.1)	9.3 (0.2)	27.6 (0.8)				

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Residual	Undigested (U) / Digested* (D)	P	K	Ca	Mg	S	M3-Na	Fe	Mn	Zn	Cu	B	Al
		(mg kg^{-1})											
RM(ar)	U	593 (23)	81 (4)	31,410 (758)	4,000 (106)	2,486 (67)	897 (42)	65 (3)	22 (2)	1,274 (54)	105 (5)	1,281 (54)	3.2 (0.1)
	D	41,735 (1,463)	83 (3)	102,504 (2,653)	5,625 (252)	5,003 (116)	1,146 (57)	258,690 (9,145)	1,641 (75)	45,605 (1,956)	2,260 ((97)	3,020 (160)	689 (42)
RM(sat)	U	2,903 (93)	15,474 (378)	17,625 (414)	4,114 (156)	2,537 (67)	742 (33)	22 (2)	39 (2)	1,105 (93)	137 (6)	1,064 (73)	3.3 (0.1)
	D	58,850 (1,987)	17,505 (483)	101,109 (2,285)	5,957 (283)	4,030 (112)	1,059 (84)	222,698 (7,947)	1,456 (61)	38,710 (1535)	1,925 (76)	2,405 (48)	604 (26)
WTR(ar)	U	9.6 (1)	79.5 (2)	355 (6)	9 (2)	87 (3)	46 (3)	45 (3)	15 (2)	5.6 (1.1)	0.8 (0.2)	1.4 (0.0)	1,799 (73)
	D	1,162 (47)	1,535 (83)	1,675 (48)	820 (24)	5,782 (137)	114 (4)	15,189 (524)	910 (42)	62 (2)	29 (2)	14 (1)	147,784 (5,712)
WTR(sat)	U	74.7 (4)	3,166 (66)	544 (17)	13 (1)	132 (4)	59 (4)	37 (2)	30 (2)	3.5 (1.4)	0.7 (0.0)	0.5 (0.0)	1,670 (85)
	D	5,287 (193)	5,832 (171)	1,681 (37)	772 (25)	5,492 (156)	114 (6)	14,668 (531)	937 (34)	60 (2)	25 (2)	14 (1)	144,577 (3,146)

545 *Digestion using USEPA Method 3050B (1 g sample weight, 50 mL total volume), analysis on Spectro Arcos ICP

546

547 **Table 2** Characteristics of soils used in incubation study (n=3, standard deviation in parentheses)

Soil texture	% sand	% silt	% clay	Water holding capacity (kg water kg soil^{-1})	M3-P (mg kg^{-1})	WEP (mg kg^{-1})	pH
Sandy loam	52.6	41	6.4	300 (20)	46.4 (2.1)	9.4 (0.2)	7.7 (0.2)
Silt loam	40	58.1	1.9	380 (25)	10.9 (1.2)	7.1 (0.5)	7.8 (0.1)
Clay loam	25.3	41.3	33.4	400 (43)	2 (0.2)	9.4 (2.1)	5.8 (0.2)

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552 **Table 3** Residual water extractable P (mg kg^{-1}) at time of application to plots during
553 runoff study. All residuals were surface applied at the rates and times indicated.

Treatment	Application 1 (2 t ha^{-1})* (day 0)	Application 2 (3 t ha^{-1})* (day 70)
RM(ar)	0.57	0.41
RM(sat)	1.39	4.03
WTR(ar)	0.06	0.01
WTR(sat)	1.24	4.60

554 *dry weight equivalent

Legend

RM(ar)	'As received' Red Mud
RM(sat)	Saturated / Partially saturated Red Mud
WTR0	'As received' Water Treatment Residual
WTR100	Saturated / Partially saturated Water Treatment Residual

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Table 4 Water extractable P (WEP), pH, electrical conductivity (EC), and Mehlich-3 extractable P (P), -calcium (Ca), -iron (Fe), -aluminum (Al), and modified degree of P saturation (DPS_{mod}) of soil samples (0-10 cm depth) taken from rainfall simulation plots six months after application of first residuals. (n=3, SD in parentheses). Differences between treatments within each group of results are not significant ($p < 0.05$).

Treatment	WEP (10:1) (mg kg^{-1})	pH	EC (µS/cm)	M3-P (mg kg^{-1})	M3-Ca (mg kg^{-1})	M3-Fe (mg kg^{-1})	M3-Al (mg kg^{-1})	DPS_{mod} (%)
Control	20.8 (1.1)	6.56 (0.03)	174 (12)	145.0 (34.3)	1487 (219)	146.5 (3.1)	392.1 (4.6)	26.9 (6.4)
RM(ar)	16.7 (1.0)	6.99 (0.44)	173 (14)	125.8 (8.6)	1246 (102)	162.5 (21.0)	478.0 (93.4)	20.1 (4.2)
RM(sat)	21.1 (1.2)	6.77 (0.44)	164 (11)	146.2 (21.3)	1374 (10)	139.6 (7.6)	389.2 (10.2)	27.6 (3.1)
WTR(ar)	16.3 (4.9)	6.81 (0.33)	153 (15)	150.0 (67.5)	1358 (331)	148.4 (4.6)	429.4 (68.7)	26.8 (14.7)
WTR(sat)	16.2 (2.2)	6.83 (0.31)	183 (27)	140.8 (24.4)	1532 (622)	146.4 (1.7)	435.0 (67.8)	24.7 (7.0)

Legend

RM(ar)	'As received' Red Mud (DPS_{mod} = 1.9%)
RM(sat)	Partially saturated Red Mud (DPS_{mod} = 16.4%)
WTR0	'As received' Water Treatment Residual (DPS_{mod} = 0.4%)
WTR100	Partially saturated Water Treatment Residual (DPS_{mod} = 3.3%)
DPS_{mod}	Modified Degree of P Saturation, defined as (M3 -P/[Al+Fe+Ca])

Table 5 Phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sulphur (S), sodium (Na), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), boron (B) and aluminum (Al) composition of forage cuttings taken immediately prior to final rainfall simulation (day 90). (n=3, SD in parentheses). Amendments are as described in Table 4. Differences between treatments within each group of results are not significant ($p < 0.05$).

Treatment	P	K	Ca	Mg	S	Na	Fe	Mn	Zn	Cu	B	Al
	%	%	%	%	%	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Control	0.44 (0.06)	2.44 (0.09)	0.59 (0.02)	0.18 (0.02)	0.38 (0.02)	98 (1)	128 (73)	59 (5)	44 (11)	10 (1)	14 (17)	29 (8)
RM(ar)	0.40 (0.04)	2.15 (0.27)	0.54 (0.02)	0.17 (0.02)	0.37 (0.03)	108 (11)	93 (12)	56 (3)	40 (7)	9 (1)	4 (3)	107 (73)
RM(sat)	0.46 (0.10)	2.14 (0.10)	0.51 (0.03)	0.19 (0.00)	0.33 (0.01)	90 (36)	240 (240)	65 (5)	66 (40)	10 (2)	12 (13)	27 (9)
WTR(ar)	0.47 (0.05)	2.35 (0.02)	0.53 (0.05)	0.19 (0.04)	0.34 (0.03)	108 (45)	134 (68)	62 (8)	46 (18)	9 (1)	14 (16)	58 (39)
WTR(sat)	0.45 (0.00)	2.20 (0.21)	0.52 (0.07)	0.19 (0.03)	0.34 (0.02)	74 (25)	79 (14)	64 (8)	33 (6)	9 (1)	3 (0)	116 (52)

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573 **Table S1** Soil pH, electrical conductivity (EC) and Mehlich extractable P (M3-P), calcium (M3-Ca),
574 iron (M3-Fe), aluminum (M3-Al) and degree of P saturation (DPS) in the sandy loam soil after 90
575 days incubation. The three target soil M3-P levels were low (50 mg kg^{-1}), medium (200 mg kg^{-1}) and
576 high (550 mg kg^{-1}). (n=3, SD in parentheses).

Sandy loam soil (M3-P)	Treatment	pH	EC (µS/cm)	M3-P (mg kg^{-1})	M3-Ca (mg kg^{-1})	M3-Fe (mg kg^{-1})	M3-Al (mg kg^{-1})	DPS_{mod} (%)
low	Control	7.8 (0.2)	60 (16)	64 (1)	1102 (1)	125 (2)	280 (2)	4.3 (0.0)
	RM(ar)	7.8 (0.1)	2590 (429)	615 (53)	7730 (1860)	140 (45)	28 (12)	8.1 (2.6)
	RM(sat)	7.5 (0.1)	2130 (177)	1410 (33)	7080 (234)	150 (50)	17 (4)	19.5 (1.2)
	WTR(ar)	7.4 (0.2)	106 (41)	34 (5)	955 (69)	87 (6)	1070 (156)	1.6 (0.4)
	WTR(sat)	7.3 (0.3)	68 (12)	99 (1)	1040 (34)	101 (12)	1210 (34)	4.2 (0.2)
med.	Control	7.3 (0.3)	106 (24)	212 (7)	1150 (98)	163 (24)	296 (28)	13.2 (1.7)
	RM(ar)	7.7 (0.1)	2790 (1150)	624 (48)	7400 (750)	143 (20)	27 (13)	8.3 (1.5)
	RM(sat)	7.5 (0.0)	3260 (643)	1440 (274)	5040 (1060)	126 (14)	11 (4)	27.9 (0.3)
	WTR(ar)	7.1 (0.5)	102 (24)	75 (6)	975 (87)	97 (3)	1160 (92)	3.4 (0.5)
	WTR(sat)	6.8 (0.0)	168 (89)	137 (12)	978 (189)	104 (8)	1230 (300)	6.0 (0.8)
high	Control	6.8 (0.0)	241 (30)	606 (37)	1250 (40)	191 (6)	310 (9)	34.5 (1.6)
	RM(ar)	7.7 (0.1)	2260 (143)	835 (96)	7290 (2150)	122 (3)	28 (7)	11.5 (2.1)
	RM(sat)	7.3 (0.3)	2500 (357)	1580 (22)	6475 (140)	182 (29)	27 (4)	23.7 (0.3)
	WTR(ar)	7.6 (0.0)	162 (13)	162 (0)	897 (128)	124 (10)	1200 (221)	7.4 (1.2)
	WTR(sat)	7.8 (0.0)	143 (39)	229 (16)	892 (97)	127 (19)	1080 (121)	10.9 (0.5)

577

Legend

RM(ar)	'As received' Red Mud
RM(sat)	Saturated / Partially saturated Red Mud
WTR0	'As received' Water Treatment Residual
WTR100	Saturated / Partially saturated Water Treatment Residual
DPS_{mod}	Modified Degree of P Saturation, defined as (M3 -P/[Al+Fe+Ca])

Table S2 Soil pH, electrical conductivity (EC) and Mehlich extractable P (M3-P), calcium (M3-Ca), iron (M3-Fe), aluminum (M3-Al) and degree of P saturation (DPS) in the silt loam soil after 90 days incubation. The three target soil M3-P levels were low (50 mg kg^{-1}), medium (200 mg kg^{-1}) and high (550 mg kg^{-1}). (n=3, SD in parentheses). Amendments are as described in Table S1.

Silt loam soil (M3-P)	Treatment	pH	EC (µS/cm)	M3-P (mg kg^{-1})	M3-Ca (mg kg^{-1})	M3-Fe (mg kg^{-1})	M3-Al (mg kg^{-1})	DPS_{mod} (%)
low	Control	7.2 (0.1)	207 (93)	63 (6)	1623 (9)	139 (7)	362 (6)	3.0 (0.3)
	RM(ar)	7.6 (0.2)	2440 (49)	638 (2)	7037 (341)	90 (0)	25 (1)	8.9 (0.5)
	RM(sat)	7.6 (0.1)	2280 (115)	1380 (318)	6117 (184)	115 (27)	35 (28)	22.1 (5.9)
	WTR(ar)	6.9 (0.0)	226 (59)	34 (3)	1234 (4)	98 (4)	1150 (39)	1.4 (0.1)
	WTR(sat)	6.9 (0.2)	217 (51)	94 (7)	1310 (134)	117 (19)	1090 (131)	3.8 (0.7)
med.	Control	7.4 (0.1)	157 (123)	168 (9)	1610 (42)	345 (13)	369 (5)	7.2 (0.3)
	RM(ar)	7.7 (0.0)	2780 (689)	716 (11)	6580 (828)	91 (2)	24 (1)	10.8 (1.5)
	RM(sat)	7.4 (0.2)	2970 (405)	1620 (289)	6790 (493)	87 (11)	28 (10)	23.7 (5.9)
	WTR(ar)	6.8 (0.1)	233 (12)	75 (4)	1330 (17)	119 (1)	1070 (54)	3.0 (0.2)
	WTR(sat)	7.0 (0.4)	247 (67)	130 (3)	1320 (17)	124 (7)	1080 (71)	5.1 (0.0)
high	Control	7.1 (0.5)	259 (98)	518 (68)	1510 (122)	372 (127)	408 (33)	23.0 (5.8)
	RM(ar)	7.9 (0.1)	2630 (28)	828 (39)	7610 (1590)	115 (16)	29 (5)	10.8 (1.7)
	RM(sat)	7.4 (0.2)	2970 (561)	1590 (68)	6010 (763)	98 (1)	28 (4)	26.0 (2.1)
	WTR(ar)	7.2 (0.3)	258 (49)	147 (6)	1310 (20)	160 (3)	1100 (11)	5.7 (0.2)
	WTR(sat)	7.6 (0.2)	297 (58)	216 (12)	1200 (143)	171 (9)	1160 (134)	8.6 (1.4)

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593 **Table S3** Soil pH, electrical conductivity (EC) and Mehlich extractable P (M3-P), calcium (M3-
594 Ca), iron (M3-Fe), aluminum (M3-Al) and degree of P saturation (DPS) in the clay loam soil
595 after 90 days incubation. The three target soil M3-P levels were low (50 mg kg^{-1}), medium (200
596 mg kg^{-1}) and high (550 mg kg^{-1}). (n=3, SD in parentheses). Amendments are as described in
597 Table S1.

Clay loam soil (M3-P)	Treatment	pH	EC (µS/cm)	M3-P (mg kg^{-1})	M3-Ca (mg kg^{-1})	M3-Fe (mg kg^{-1})	M3-Al (mg kg^{-1})	DPS_{mod} (%)
low	Control	6.2 (1.0)	84 (24)	25 (1)	1210 (20)	59 (8)	1040 (11)	1.1 (0.0)
	RM(ar)	7.7 (0.0)	2680 (358)	681 (15)	11400 (837)	61 (63)	361 (12)	5.8 (0.2)
	RM(sat)	7.0 (0.0)	5200 (3600)	1530 (41)	9230 (491)	75 (42)	341 (4)	15.8 (0.3)
	WTR(ar)	6.4 (0.2)	88 (24)	12 (1)	1070 (102)	39 (1)	1340 (71)	0.5 (0.1)
	WTR(sat)	6.8 (0.5)	167 (135)	49 (0)	1010 (31)	46 (2)	1320 (18)	2.1 (0.0)
med.	Control	5.7 (0.2)	103 (21)	126 (4)	1080 (60)	74 (3)	982 (4)	5.9 (0.4)
	RM(ar)	7.7 (0.0)	2950 (116)	760 (73)	10800 (424)	110 (15)	344 (57)	6.7 (0.4)
	RM(sat)	7.2 (0.0)	2700 (52)	1690 (394)	8870 (732)	79 (2)	312 (88)	18.2 (3.0)
	WTR(ar)	6.7 (0.2)	95 (8)	43 (2)	1060 (71)	46 (1)	1360 (0)	1.7 (0.1)
	WTR(sat)	6.9 (0.2)	72 (4)	81 (2)	1030 (82)	50 (1)	1320 (76)	3.4 (0.3)
high	Control	5.8 (0.0)	158 (6)	473 (11)	1000 (16)	134 (3)	997 (7)	22.2 (0.6)
	RM(ar)	7.7 (0.1)	2930 (129)	910 (12)	10700 (505)	82 (11)	331 (9)	8.2 (0.5)
	RM(sat)	7.1 (0.0)	2640 (158)	1660 (331)	8250 (192)	132 (8)	332 (52)	19.0 (3.5)
	WTR(ar)	6.8 (0.0)	120 (12)	130 (4)	934 (9)	66 (1)	1250 (8)	5.8 (0.2)
	WTR(sat)	7.3 (0.0)	82 (20)	162 (21)	969 (83)	73 (3)	1310 (107)	6.9 (1.5)

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